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EDITORIAL

Miracles of Chemistry

WE have stolen this title from *The Times* of Monday last, as many will know who have read that well-considered editorial article on the latest "miracle" of science, the production of sugar from wood. Following Dr. Bergius's address to the Institution of Chemical Engineers there has been in the daily papers much comment on the wonders of modern chemistry. So, every now and again, does the chemist come into his own for a little while, and it is by such conjuring tricks of chemistry that he is most easily able to do so, whether it be by making colours of the rainbow from coal-tar, umbrella handles from milk, petrol from coal, fertilizers from air, or—sugar from wood. These are indeed wonders, even for those of us who are able to see the relationship of things which superficially are unconnected. and although we may always be expecting the appearance of another rabbit we are none the less delighted when it comes out of the hat. We have, in fact, "grown wiser, and yet lost not wonder." But to call such things miracles seems to be overstating the case. We see many substances with an analytical eye, and seeing something if not everything of their constituents, our imagination prepares us for possible rearrangements of those constituents. New products for old, old ones from new, they are all there for the making, and it needs simply the advent of a Perkin or a Haber, a Baekeland or a Bergius, to make the foreseen an accomplished fact. That human ingenuity can contrive such changes, bringing Jules Verne's books to life and making H. G. Wells seem logical rather than imaginative, must always be a matter for some wonder, if temporary, but for scientists there can be few miracles within the domain of science. There is, we confess, a certain passage in Brahms' "Variations on a Theme of Haydn" that by its complete serenity can make the worst tolerable and the good infinitely better, and similar miracles for us can be achieved by the César Franck symphony and the slow movement of a Debussy quartet. Who has not felt a similar atmosphere of something beyond wonder on reading or hearing some lines of poetry? There was a moment a week or two ago when we looked down on Finsbury Square to see the traffic stilled and men motionless, and there was no sound for two minutes but the rustling of a few forlorn leaves, and there seemed something of a miracle in this. There was another occasion, still more recent, when we took a road from Downe, a road that Darwin must have known, that in course of time wound its way over a hill, with many beeches on either side: a little later and the road itself was hardly to be seen for its carpet of chestnut leaves; and finally the road came out of the woods and before us was a landscape we have seen a dozen times but which for the moment was unbelievably beautiful. Miraculous to us, it must seem commonplace to others. We live in an age that confuses the miraculous, the phenomenal, the sensational, and the wonderful. Although, if we may quote Chesterton again, "there is one sin, to call a green leaf grey, whereat the sun in heaven shuddereth," a more common sin nowadays is to call a grey leaf green, making much of many things that are not worth our wonder. Sometimes man has gone hand in hand with Nature, and together they have achieved many things, and when Nature, which is not always benign, has been against him, things no less remarkable have been accomplished. A modern Rip Van Winkle might find much cause for astonishment, but if he should happen to be a scientist he would find few miracles. For those we must perhaps wait until man has stayed katabolism and death and has learned to create life.

TWENTY YEARS OF PETROLEUM RESEARCH— A RETROSPECT*

By Dr. A. E. DUNSTAN

Introduction

I purpose in this address to give you some personal reminiscences of my own experiences and experiments during the past two decades, because I think on such an occasion as this it is interesting to look backwards as well as forwards, and because the story of the attempts made, the successes achieved, and the failures mourned over are of value to those who are now in the firing line of effort.

This past 20 years is a period of outstanding interest in our profession. During it has occurred the Great War—with a revolutionary impact on the petroleum industry. It has seen the formation of great associations such as the American Petroleum Institute and the Institution of Petroleum Technologists. It has seen the change over from "rule-of-thumb methods" to strictly scientific procedure. It has seen the replacement of untrained personnel by men of university upbringing, and the application of scientific thought and method throughout its whole range of endeavour. It has seen the establishment of vast research organizations throughout the world. During my own 20 years' association with mineral oil—most of which has been spent with the Anglo-Persian Oil Company—I have witnessed the birth of a research department and have been largely responsible for its upbringing. I can look at it to-day as a flourishing and vigorous unit. I would be ungracious if I did not express here and now my appreciation of the part played by my chief, Sir John Cadman, in fostering, maintaining, and stimulating the scientific life of our own organization.

It is remarkable, looking back over this period of time, to realize how relatively simple petroleum refining was. Distillation was achieved in shell stills—some continuous on the Henderson plan, many more on the batch system. The water-tube boiler had found few imitators, and yet I can remember a tubular still that processed coal tar—invented I think by Lennard—that was working at the South Metropolitan Gas Works, Greenwich, over 30 years ago. That useful maid-of-all-work, sulphuric acid, was the universal refining agent. Scottish shale-oil practice, originated by the work of James Young, still occupied the forefront in petroleum treatments. In the Eastern refineries colour in kerosene was an advantage, and water-white burning oil was viewed with suspicion. Much machinery was lubricated with fatty oil—olive in particular. The asphalt road was scarcely known in our great cities, although the Thames Embankment had been laid a long time by Clifford Richardson, and Maybury had introduced tar spraying in Kent. The middle distillates of the gas-oil class were solely used in the coal-gas industry for enrichment purposes. Octane rating was unheard of. the problems of the high-speed high-efficiency gasoline motor had not arisen. Cracking was, indeed, talked about; Redwood had shown that gas oil could be cracked to kerosene, and the Russian operators had contemplated the production of aromatic hydrocarbons in the like manner. Vapour-phase cracking appealed to most oil men, and the earliest experiments in the war time for the obtaining of toluol are of historical interest to-day.

One of my very first problems was on such a process. The plant was that of Hall, the conversion temperature was 750° C. The pressure was only a few atmospheres. Distillate from Persian residue—gas oil and wax distillate about 80% of the fuel and about 50% of the crude—was the charging stock. Of the liquid cracked product some 16% was toluol, but the pressure distillate was so complicated, and there was such a high content of very reactive hydrocarbons, that the isolation of the pure aromatic hydrocarbon was commercially impossible and could it have been successfully separated, the final cost would have been prohibitive. The failure of this process synchronized with the commercial and very big-scale production of toluol from Borneo benzene by good fractionation followed by the mononitration of the contained toluene. It is of interest to note that natural petroleum toluene completely overshadowed that produced from coal tar in the United Kingdom. If the same problem occurred to-day, it would be interesting to see how our oil technologists would tackle it. I shall indicate later some possibilities in this direction.

I think it will be convenient to discuss the various sections of my retrospect by subject matter rather than chronologically. Consequently, I shall trace our endeavours, in the first instance, to

Natural Gas

I remember in my first visit to Persia, 18 years ago, being oppressed by the magnitude of our gas problems. The Masjid-i-Suleiman field was then in the early stages of development. We were faced with a high gas–oil ratio, and withal a rich gas and a highly poisonous gas. The content of hydrogen sulphide was upward of 12%. Some time lapsed before the gas was harnessed and the gasoline content recovered. Long before all this had occurred, I had been interested in the possibilities afforded by the thermal decomposition of the lower-paraffin hydrocarbons and 14 years ago preliminary experiments were carried out. A little later the welcome co-operation of Prof. Wheeler of the University of Sheffield was secured, and the mass of information collected by his research school in this field was placed at our disposal. This work has recently been discussed at the Chicago convention of the American Chemical

* Paper communicated to the Ottawa Section and the American Petroleum Institute in October, 1933.

Society, and need not be detailed now; but in brief the results of the work may be summarized as follows:

The main processes worked out have been:

(1) Pyrolysis for the production of motor benzol;

(2) Pyrolysis for the production of olefin hydrocarbons;

(3) Polymerization and condensation of olefins to give low-boiling liquids.

From a consideration of the paraffin hydrocarbons, ethane to hexane, it was found that, in the primary decomposition, rupture of the chain can take place at any position producing an olefin and the complementary lower paraffin or, at the limit, hydrogen. The absence of a C-C linking in methane causes this gas to differ from the catenary in paraffins, and the suggested mechanism is $CH_3{\cdot}H \rightarrow {:}CH_2 + H{\cdot}H$ and $2CH_2{:} + H_2 \rightarrow CH_3{\cdot}CH_3$.

With the gaseous mono-olefins the principal primary reactions—common to all—involve the formation of either the two-carbon or the four-carbon (or both) atom members of the olefin series. If conditions are drastic, an important secondary reaction is the decomposition of butylene to give butadiene and hydrogen.

The paraffin hydrocarbons, with the exception of methane, exhibit a range of 700° C. to 750° C., in which the production of ethylene reaches a maximum under the particular experimental conditions employed. Evidence indicates that ethylene is the source of the aromatic hydrocarbons produced above 750° C. A mechanism for aromatic-hydrocarbon production was developed from ethylene via butylene, butadiene, and cyclohexene to benzene. The presence of styrene, naphthalene, and anthracene is readily accounted for in this scheme.

Tables I and II summarize the experimental results:

The liquid hydrocarbons produced contain benzene, toluene, the xylenes, styrene, indene; whilst the tar contains indene, naphthalene, anthracene, and phenanthrene.

It was shown further that the first stage in the reactions involved—when ethylene is heated at atmospheric pressure—is a polymerization to butylene. The influence of pressures in the range 200 to 2000 lb. per sq. in. has been considered in the temperature region 300° to 600° C., and under these conditions liquid hydrocarbons can be produced from the gaseous olefins. The conversion is high (92% under suitable conditions with ethylene) and the production of by-products and carbon can be kept low. Ethylene, propylene, and mixtures of these gases have also been considered, together with the influence of saturated diluents such as hydrogen, methane, and ethane.

Using ordinary mild steel and copper surfaces violent decomposition of ethylene, resembling the flashing of acetylene, accompanied by a copious deposition of soft carbon, occurs at times. This may be obviated by the use of special metal liners.

The liquid hydrocarbons produced during polymerization vary with the operating conditions, but the usual product has a specific gravity of 0·77 at 15° C., and contains 86% volatile below 200° C. The distillate below 200° C., as an anti-knock fuel, is about five-sixths as good as benzene on a volume basis, and rather better than benzene on a weight basis.

In order to apply polymerization and condensation processes to natural-gas hydrocarbons it is necessary to produce therefrom olefins in a low-pressure mild-pyrolysis operation.

The above summary indicates that this line of work is exceedingly promising. In fields where the direct

TABLE I

Pyrolysis of the paraffin hydrocarbons for the production of aromatics at atmospheric pressure

Gas	Temperature (° C.)	Conversion into liquids (% by weight)	Conversion into distillate boiling below 170° C. (%)	Gallons per 1000 cb. ft. total oils	Gallons per 1000 cb. ft. distillate boiling below 170° C.
Methane	1050	8·8	5·0	0·44	0·25
Ethane	850	17·93	11·2	1·7	1·1
	900	21·9	10·63	2·1	1·0
Propane	850	23·09	11·65	3·25	1·6
Butane	800	20·4	12·91	4·0	2·4
	850	24·55	11·64	4·6	2·35
Pentane	850	26·8	11·87	—	—
Hexane	800	33·7	19·2	—	—
	850	33·8	19·0	—	—

TABLE II

Pyrolysis of the olefin hydrocarbons for the production of aromatics at atmospheric pressure

Gas	Temperature (° C.)	Conversion into liquids (% by weight)	Conversion into distillate (% by weight)	Gallons per 1000 cb. ft. total oils	Gallons per 1000 cb. ft. distillate
Ethylene	800	36·1	17·7	3·15	1·6
Propylene	750	35·6	20·4	4·7	2·75
	800	40·6	19·0	5·32	2·5
Δα butylene	700	35·8	23·6	6·25	4·1
	750	39·6	22·45	6·85	3·95
Δβ butylene	700	37·0	25·8	6·4	4·45
	750	39·6	23·2	6·85	4·1

tilization of gas is difficult, and where transport of gas ; impossible, pyrolysis affords a convenient method of ·onomic disposal. Attached to the conventional (and specially high-temperature) cracking units, the olefin ontent of the cracked gases may be practically quantitavely converted into high anti-knock fluid hydrocarbons. he survey of gas yields and compositions from a variety ' cracking units has shown that, in certain cases at latively high temperature of operation, the gas "loss" ay reach so high a figure as 30%, containing 50% of efins. The procedure outlined above, obviously, ould reduce the loss to 15%, and add the balance by eight as liquid

Many other gas problems have been worked out: for ample, the isolation of the hydrogen-sulphide content d the conversion into sulphuric acid, determination of ysical constants, investigations on the gas oil ratio, ubility relationship, and a variety of questions relating production.

CRACKING

I have already spoken of our early experiences with the ll vapour-phase process, and it is not without interest note that this type of cracking operation is still attract- g attention—chiefly, I suppose, because of the high ti-knock rating of its product.

Undoubtedly, the earlier cracking methods had in ew the quantity production of gasoline: to-day, her, is the tendency towards quality cracking—and s tendency may well influence all future develop- ents. No doubt also the pioneering vapour-phase ocesses ceased to operate because of heavy gas losses d the real difficulty of efficient and economical refining the fuel. Quite early we devoted much attention to uid-phase operation, and both Dubbs and Cross units re installed in our South Wales refinery, and recently very large Kellogg plant was put into our Abadan inery in Persia. It is interesting to look back and see w the whole gasoline situation has changed during the iod under review. Anti-knock rating is to-day the tstanding criterion, and the race for ultra-high engine ciency makes ever-increasing demands on the refiner. e available supply of straight high-octane-rating gaso- e is very limited, and indeed the world's most prolific ds are not distinguished in this respect. Hence, the velopment of the reforming of light distillates: and does seem likely that the cracking unit of the future l largely be devoted to this end—more especially when impact of the high-speed Diesel engine on the domain the gasoline motor is considered.

We have carried out a considerable amount of research a model visual cracking apparatus that has already n described in the literature (Ind. Eng. Chem. 1929, 643). This miniature plant enables conditions emperature and pressure and of time to be determined a given degree of cracking, and has proved of great ue. Small semi-scale plants have also been con- icted, and in particular one that comprises a pipe l in which conditions of turbulent flow can be main- ned by the superimposition of an alternating high- ocity surge. It is clear that each particular crude its own special attributes—and difficulties—and as been of the utmost value to us to be able to discover the optimum working conditions on our own material, having regard to the product demanded.

Side by side with experimental work on cracking has proceeded the elucidation of the problems of the adequate refining of the gasoline. At a very early stage in our work came the development in our laboratories of a counter-current continuous washing apparatus which was a direct adaptation of a method that had been invented for the continuous production of T.N.T. This very admirable and effective system depends on the difference in density between an emulsion and the components of the emulsion, and it can readily be seen that the difference in density can be converted into a flow of the separated materials, *e.g.*, acid tar and gasoline. The energy of stirring becomes energy of translation. It is unnecessary here to discuss the obvious advantages of counter current treatment—but they are especially apparent in handling reactive substances like cracked gasolines.

Acid washing on this system has been applied to all our pressure distillates, followed by re-distillation and sweetening; but more will be said of this side of the operation when discussing the refining of straight gasolines. After many years' work the acid treatment of cracked distillates still holds the field. So long as the conflicting necessities of reduction in gum and colour with a minimum reduction of engine rating can be reconciled, acid is the simplest and most effective agent to-day. It is likely, however, to lose its place if the active development of catalytic treatments proceeds. Such work as that of Lachmann is of promise. We, some time past, developed a method on somewhat similar lines, but using a carrier for the zinc chloride; whilst early research on the application of aluminium chloride goes back to 1918.

Mention should be made at this stage of the work carried out on inhibitors. The ever-pressing necessity of maintaining the full anti-knock value of cracked gasoline has caused special attention to be given to gum-inhibiting material: and it is not without interest that such material may actually be inherent in the crude oil. A divided treatment has also been worked out wherein the lighter end of the cracked distillates may be dealt with for gum, and the heavier for colour removal. It does seem appropriate here that I should refer to the unnecessary stress put upon the physical properties of gasoline, and especially colour. The refiner has to face losses and costs not commensurate with the advantages conferred upon his product. I very much doubt whether the high-speed Diesel will ever be fueled on such a super-refined material. It is not inherently impossible to design a fuel system for the automobile such that the consumer will never see or smell the fuel. All that is needed is chemical and physical stability, volatility, and anti-knock value. I well remember in the war driving on the forerunnings of a benzol rectification plant that contained 60% of carbon disulphide, and without any unpleasant happenings. The public has been spoiled.

I do not purpose to discuss in any detail the prolonged investigation we made into the nature of the sulphur derivatives present in our own crude and the development of the hypochlorite process. That has been done already, and can be found in the text-books. But this occasion does give me the opportunity of referring to the happy collaboration that was brought about by this

work. I refer to our joint research with B. T. Brooks, and out of that arose our many other connexions in America—contacts that commenced in a common interest in technology, that were initiated by common efforts in the laboratory and refinery, and that have in so many cases fructified into lasting friendships. May I just mention the names of Egloff, Peters, Wilson, Isom, Haslam, Edgar, Boyd, Fröhlich, Anderson, Mackenzie Delbridge, Hill, Whitby, and so many other good friends with whom I am so proud to be connected.

And, furthermore, this leads me to acknowledge the courtesy of your great associations—the American Society for Testing Materials, in which I have the honour and privilege to be honorary chairman of the D-2 committee; the American Chemical Society, and the American Petroleum Institute.

There is, however, a point in gasoline refining that is of recent interest, and that is in connexion with the effect of sweetening agents on anti-knock and lead response. All the evidence does seem to indicate that plumbite may yield catenary *thio*-derivatives that in some way interfere with tetraethyl lead. Observations have been already published on this matter, and it is still under review.

Looking back on two decades of experimental work on the chemical treatments of gasoline, it is amazing to contemplate the vast amount of effort that has been expended. I remember sulphur content being reduced to 0·01%, and a degree of refinement that is really absurd being regarded as commonplace. It was due to the divorcing of specifications from common sense. We are in a somewhat happier position to-day, in that scientific common sense is being applied to the education of the consumer, but let us all beware of forging fetters for ourselves that have only one real object—that of providing sales talk. I shudder when I hear of a new test being put forward. I rejoice when yet another test is declared obsolete. I welcome the efforts made to bring about a simple international code of testing.

Kerosene Refining

In my earlier experiences we used in our Persian refinery a combination process: first, a plumbite sweetening, and then a decolorization and final polish by means of ignited bauxite. This latter process was invented by Hood. Our first experiments showed that bauxite did far more than decolorize. It was an excellent desulphurizing agent—although the amount wanted was large. In point of fact such ratios as 4 lb. per gal. were needed. The action of these mineral gels was interesting scientifically, and we spent a considerable time on investigation that showed a dual operation—each section of which followed the well-known adsorption law of Freundlich, as applied to decolorization and desulphurization. Some experiments were even made on the refining of lubricating oil. Bauxite is now largely superseded, but still finds a use for the ultimate polish of special kerosenes.

Very interesting are my recollections of the Edeleanu process. Just before the war our friends, the Burmah Oil Company, were investigating the then remarkable claims of Edeleanu for the refining of kerosene. I was attracted from a different angle, viz., the use of liquid sulphur dioxide as a solvent for toluol and as a means of extracting toluol from gasoline for munitions purposes. A little later we considered it as a means of refining lubricating oils. As is well known, the process has achieved a secure place in petroleum technology; and in its later development, associated with benzol, appears certain to play an important part in lubricating-oil technique. It is interesting to recollect that at your meeting in 1928 I suggested that Dr. Edeleanu should speak to you on the avoidance of acid sludge by the utilization of his process.

Engine and Fuel Research

It has already been indicated that the whole picture of engine performance has radically changed in the period of my recollection.

During recent years internal-combustion engines, both for light and heavy fuels, have undergone such developments in design that they have ceased to be omnivorous. For example, the low-compression motor-car engines of 1925, which could utilize straight-run gasoline satisfactorily, now have compression ratios at least 30% higher and, consequently, develop considerably greater power without any change in gasoline consumption. This high compression means, however, that despite compensating improvements in design, such as the Ricardo turbulent head and the synchronized dual ignition, such engines will very rarely burn straight-run gasoline at full throttle without "pinking." Consequently, motor fuels have changed correspondingly, and now there is little straight-run unblended gasoline on the market.

The study of the behaviour of fuels during this combustion in a cylinder has become of high importance in the last few years, and the advances in the quality of both engines and fuels could not have been made without intensive research on this subject.

Very many lines of research and routine work opened up by the use of experimental engines will be readily apparent. A few of the more prominent may be stated:

(1) Pure research on the mechanism of flame propagation and the cause of "pinking."

(2) Study of the anti-knock or pro-knock properties of individual hydrocarbons and the correlation of these with chemical structure.

(3) Study of the anti-knock or pro-knock properties of "dopes" and also of non-hydrocarbon fuels such as alcohol.

(4) Search for various alternative sources of anti-knock ingredients for motor fuels. Natural gasoline, cracked hydrocarbons made by various processes, natural and synthetic aromatic hydrocarbons, and especially-selected natural petroleum are included in this section.

(5) Production of special fuels for aviation and racing purposes.

(6) Study of the effect of the various details of engine design, such as spark-plug settings, valve settings, turbulence, mixture strength, internal and external temperature, ignition setting, etc. on the combustion of the fuel.

(7) Examination of the influence of climatic conditions (air temperature, humidity, and atmospheric pressure) on detonation.

A further series of investigations is opened up as regards Diesel engines, such as:

(1) The effect of constituents such as sulphur, asphalt, and wax on the combustion of the fuel and on the engine.

(2) The behaviour of fuels of various chemical types, such as naphthenic oils, paraffinoid oils, coal tars, residuum versus distillate oils in Diesel and semi-Diesel engines.

(3) The effect of engine design as regards essential factors such as injector nozzles, combustion space, hot bulbs, timing of injection, etc. on the combustion.

It is clear that a study of these matters is of vital importance, and will be the work of years. It has necessitated a well-equipped engine research department—which might more correctly be termed a research department of fuel combustion. Such a department has been brought into being at our research station. The building is equipped with typical motor-car, lorry, and motor-cycle engines—complete with dynamometers and special accessories for research.

It is interesting to recollect that at about this time your own C.F.R. committee was at work. In my visit here in 1930 I had the privilege of taking part in its deliberations with my English colleagues, Mr. Kewley of the Asiatic Company and Dr. Garner of the Anglo-American Oil Company. We had the opportunity of seeing the birth of the octane rating, and I well remember Graham Edgar's exposition of its merits. We, on our side, had carefully considered this important question; and we had the opportunity of hearing Dr. Dickinson on several occasions. I think it can fairly be said that our co-operation was of value. At any rate we have adopted octane ratings and C.F.R. technique, and have done our utmost to help along the good work of international standardization in this most essential criterion of performance. A few words may be given to this subject.

A thorough examination of various methods of determining anti-knock rating in conjunction with the Asiatic Petroleum Company, the Anglo-American Oil Company, and the Detonation Sub-committee of the American Society of Automotive Engineers was undertaken in 1929.

Suitable fuels were exchanged so that ratings could be obtained on the many types of test engine in use by various laboratories, and analysis of the results indicated, in no uncertain manner, that it is essential to use an agreed standard engine for inter-company correlation. The American committee wisely decided that the best policy was to design an entirely new plant, and to base this design on the experience of all important users of existing test engines. During the development period we sent representatives on two occasions to the U.S.A.; once to the Chicago meeting of the Society of Automotive Engineers, and once to the Detroit meeting. In addition, H. C. Dickinson, Chief of the Heat and Power Section of the U.S. Bureau of Standards, Washington, visited Sunbury, and also attended in London a committee meeting at which he gave a summary of the position then obtaining in America. Since that date the Institution of Petroleum Technologists has formed a sub-committee to deal with this subject.

The standard engine, known as the C.F.R. or Horning engine, is now available for general use; and its advent makes possible accurate correlation of engine tests of motor fuels in all parts of the world.

One of the most important decisions, which has made such a standardization possible, is the agreement to use as fundamental fuels the two pure hydrocarbons, *n*-heptane and *iso*octane. Any motor fuel in general use may be matched for anti-knock value by a suitable blend of these two materials, and the percentage of *iso*octane required in such a matching blend is used as a measure of the anti-knock value of the spirit under test. This percentage is referred to as the "octane number," and octane numbers are now always given in conjunction with any anti-knock test.

The need for applying the technique of knock rating to aircraft fuels opened up a new line of research for such engines which operate under somewhat different conditions from motor-car engines.

The problems presented by the use of fuels in heavy-oil engines are necessarily complicated by the very wide range of fuels which may be used and by the large number of different types of engines involved. Large air-injection Diesel engines, and, in general, large oil engines, operating at moderate speeds, are capable of using the widest range of fuels; and engines of this type may be found operating successfully on petroleum products extending from the kerosene fractions to heavy residuals. In addition, fuels such as those derived from coal tar or of vegetable origin are used.

Within recent years, however, the heavy-oil-engine field has been considerably extended, and notably in the direction of small power units of the type which are tending to displace kerosene or gasoline engines in marine, traction, and small stationary plants. There is also a tendency towards a general increase in speed and the adoption of airless injection, and the whole development calls for a more critical examination of fuel characteristics and fuel behaviour under engine conditions than was previously necessary.

Slow-running engines of large power, working at constant speed, undoubtedly show differences in fuel requirements according to type; but such differences are more under control, and the conditions are usually such that adjustments to blast air pressure or fuel valves may be made to suit the particular fuel in use.

The small high-speed engine is frequently called upon to work under less favourable conditions than the larger type. Wide variations in speed and load may be necessary—as in the case of a vehicle engine—and the small size of the unit definitely precludes the possibility of the skilled attention that can be given to the larger plant.

The present situation is somewhat similar to that which existed in relation to gasoline about 12 years ago when Tizard and Pye and Ricardo commenced their investigation of the behaviour of motor fuels. Prior to that time the phenomenon of pinking was known, but there was little information regarding its connexion with fuel classification or its effect on engine output; nor was the relation between compression ratio and efficiency established on a practical basis. Since

that date research on the lighter-hydrocarbon fuels has been carried on in an intensive manner throughout the world (principally in Great Britain and America); and a point has now been reached where the formulation of an international method of testing these fuels for anti-knock value in a standard testing engine is in active progress.

The Process of Combustion

Ricardo has pointed out that the process of combustion in a Diesel engine may be divided into three more or less distinct stages:

(*a*) The delay period between the beginning of injection into the cylinder and the commencement of pressure rise above the compression line.

(*b*) A period of rapid and almost uncontrollable combustion, during which the fuel already injected burns.

(*c*) A further period, during which the remainder of the fuel injected at the nozzle burns at a rate controlled by the pump and nozzle.

We have used the following terms for the various stages of the combustion period.

"Delay period" signifies the period between injection and the beginning of pressure rise, and is more definitely specified as "delay angle" when expressed in terms of degrees of crank angle, and "delay time" when expressed as an absolute time. The unit of time adopted is the micro-second.

"Break-away" is used to denote the point at which the combustion line leaves the compression line.

Instead of the term "detonation" we prefer to use the words "combustion shock," since "detonation" has a definite physical meaning, and may not—in the true sense—occur in engines.

Effects of Dopes

Many attempts have been made to improve the delay time and to reduce the combustion shock of certain fuels by the addition of suitable dopes. The essential characteristic of such materials is that they shall have a low self-ignition temperature at the pressure of injection; and, while we have not been able to make an exhaustive research, a few substances have been examined which, although not commercially practicable, are known to be effective. Amyl nitrite, acetaldehyde, and benzaldehyde may be employed for research purposes—although the cost of the first named, the low boiling point of the second, and the rapid decomposition of the third prevent their practical use.

A paper of this description would be incomplete without further reference to the behaviour of motor fuels as regards pinking in spark-ignition engines, and the relation between such fuels and those which give the most pronounced combustion shock in compression-ignition engines.

In recent years a large number of pure volatile hydrocarbons have been tested for anti-knock value in suitable gasoline engines, and definite relations established between tendency to knock and the chemical composition and structures of the molecule. It is, however, quite impossible to give anything approaching an accurate estimate of the knocking tendency of motor fuel from a chemical examination.

The problem with regard to heavy oils is much more complex, both on account of the highly-complicated nature of the fuel structure of the various classes of hydrocarbons present, and also because of the greater number of engine variables which can be introduced.

It is, therefore, safe to prophesy that the rating of heavy oils for Diesel engines, as for gasoline engines, must include suitable engine tests. It can be stated with a fair degree of certainty that heavy oils obtained from crudes which give motor fuels of the highest anti-knock value will be the worst from the point of view of combustion shock in a Diesel engine, and that those from crudes giving relatively low anti-knock value straight-run fuels will be comparatively good.

Diesel Oils

Unlike motor-fuel tests, the examination of Diesel-engine fuels is a comparatively undeveloped branch of fuel research, and almost every aspect of fuel behaviour in Diesel engines has needed investigation.

When the high-speed Diesel engines were installed, it became a matter of importance to secure the best-known means for examining the exact nature of the pressure changes which occur in engines during combustion: and a Farnborough indicator was employed for this purpose. This instrument has proved exceedingly valuable, and very little progress could have been made without it. It enables the behaviour of heavy oils in engines to be analysed with great accuracy, and may be said to occupy the same place in heavy-oil tests as the bouncing-pin indicator does for gasoline tests.

The ideal Diesel-engine fuel should have as many as possible of the following characteristics:

It should ignite easily to give easy starting. The burning should proceed smoothly, so that the engine runs without undue noise from combustion shock. The combustion should finish early in the expansion stroke, to avoid a smoky exhaust. The fuel should flow easily at all normal operating temperatures, but should not be too thin—or excessive leakage will occur from pumps and spray valves. Freedom from even small amounts of solids in suspension and from water is important, and the oil must not corrode the working parts of the fuel system. Carbon formation must be negligible.

The relative importance of these factors differs from one type of engine to another, and for this reason it has been essential to have a sufficient number of engines to be broadly representative of the classes in general use.

The research necessary to establish this conclusion has led to the development of routine tests to determine the relative value of any fuel in a given class of engine, and there is no doubt that engine tests of heavy oils will increase rapidly in importance.

Fuels obtained from coal by either high or low-temperature carbonization processes have proved very unsatisfactory in almost every respect for Diesel-engine use.

The growing importance of high-speed Diesel engines for transport is making a marked difference in the attitude of users towards the type of fuel supplied, and the position of paraffin-base fuels is a very satisfactory one in this respect.

It is of interest to note that the use of cetene and ıethyl naphthalene as opposite numbers to heptane nd *iso*octane appears likely to afford a comparison etween the various Diesel fuels. On the other hand, 'e have found that an aniline-point determination is not ·ithout value. The Diesel situation has always ıterested me. The obvious advantages of the compression-ignition engine are:

(1) Relative freedom from fire risk
(2) Much greater thermal efficiency
(3) Complete absence of carbon monoxide from the chaust gases
(4) Greater simplicity of operation—absence of agneto or coil- -spark plugs, and carburettor
(5) Relatively cheaper fuel—less refining—no cracking
(6) Wider range of fuel on a given crude—in effect, om kerosene to heavy distillate.

All these indicate that the truck, tractor, and bus of ıe near future will be operated by the compression-nition engine, and not the gasoline engine. In Europe is situation is developing rapidly. I can foreshadow ıat none but the small and light automobiles will ›erate on gasoline. I know of cases where a gasoline otor has been exchanged for a high-speed compression-nition engine, whilst the experience of our large bus mpanies has shown the definite superiority of the iesel cycle. Shall we see in our time the cracking or forming of light- into heavy-distillate fuels?

Colloids

An aspect of petroleum research that has always terested me is concerned with the colloidal phenomena sociated with crude oil and certain of its products and eatments. Reference may be made to Jerome Alexıder's recent work on colloid chemistry, where I have scussed certain phases of the subject; and I cannot lp feeling that there is yet to be done a vast amount work on this borderland of physics and chemistry. e have touched on the colloidal structure of certain ıraffinoid crudes and heavy residue therefrom, the *agulation of dispersed asphaltic material*, the *curious* anges in viscosity and set point of residua and hystesis effects in general, the behaviour of tar fog, the sorption relationships afforded by bauxite, floridin, ıys, and gels in general polymerization effected by nilar agencies, emulsion breaking and emulsion formg, the effect of free fatty acids and similar oxygenated mpounds on the surface tension of lubricating oils, otective colloids in wax removal and in mineral jellies, aps in lubricating-oil greases, graphite in lubricants, ıd the vast subject of asphalt emulsion and the asphalt ad. All these phenomena have at various times come our notice, and some have received experimental ›atment; but it is safe to say that further research awaiting the petroleum industry in this fertile and ıcinating field, and especially in the domain of lubricıon.

International Co-operation

The importance of international co-operation in the ›thods of testing petroleum and its products has always en closely in my mind. I have attempted to help this ›d work along for many years past, and it is largely ing to the close co-operation of your own American ›iety for Testing Materials, our Institution of Petroleum Technologists, and the International Standards Association that success has come within reach. At our World Petroleum Congress recently held in London there was an absolute unanimity of feeling that machinery existed, and could be brought to bear, on this very thorny and controversial matter. It has always been a pleasant thought that these contacts which I have striven to make effective have so successfully operated in this direction. Special thanks are due to Dr. Anderson for his efforts to bring about a practical solution of the many difficulties that existed. I am sure that the president and council of the Institution of Petroleum Technologists would wish me to present their friendly greetings on this occasion.

Conclusion

Naturally, in a series of reminiscences of this sort, one is inclined to emphasize the high spots of one's own interest. On looking back, however, I am astonished at the multiplicity of the problems that have come before us—some solved, many yet unsolved. To take only a few examples: the multifarious aspects of corrosion, both of running units and standing plants and installations, lines, and ships; the many attempts to catalyze familiar reactions; the efforts toward the synthesis of some desired compound; the preparation of innumerable derivatives: the determination of vast numbers of physical constants, many urgently desired for effective plant operation; investigations on the spot at field and refineries: the development of new products and the furthered application of those already known; in general terms, the application of science to a great and growing industry.

An aspect of the general layout of research organization that is of first importance is the clear necessity of carrying out work of purely scientific and fundamental interest. This is not only a stimulus to the staff engaged on it, but is of a definite ethical value. Too often an enthusiastic researcher is dampened somewhat on encountering the daily "bread-and-butter" problems. To such an one an incursion into the realms of pure research is really essential. Consequently, I have always endeavoured to have on the stocks, so to speak, a few problems of a general type—such, for example, as special synthesis of hydrocarbons, the isolation and characteristics of *thio*-derivatives and the like, the reactions of selected chemical entities, the determination of special physical constants and relationships, the physical and colloidal nature of lubrication, etc., which not only provides a sort of scientific "uplift" in themselves but serve to whet the curiosity and interest of the whole staff.

One of the outstanding features of the period under review has been the foundation of great research organizations and schools of petroleum research, where graduate and post-graduate courses can be undertaken, with the result that the personnel of the industry to-day is infinitely better trained for its work than was the case in the past.

In the inception of such university departments the major oil companies have shown great public spirit and foresight. These departments react on the industry in two ways: first in the provision of skilled personnel whose education has been based on sound fundamental

principles; and, second, for the furtherance of research in the investigation of problems somewhat outside the scope of the industrial research laboratories.

In my own experience and recollection I can quote particularly the case of the University of Birmingham, England, where the School of Petroleum Technology has been under the direction of Prof. A. W. Nash, who is in the fortunate position of having graduated in the petroleum industry, both at home and abroad, before returning to academic work, for the last eleven years.

This school was founded by Sir John Cadman some 20 years back, when he was professor of mining at this university, and in 1920 the department was liberally endowed by several large British oil companies in order that those desirous of entering the petroleum industry might receive a sound education in those fundamental principles which underlie the science of petroleum technology.

This school has been responsible for placing in industry a large number of men, many of whom have risen to positions of responsibility; and there is probably not an oil field or refinery in Europe and the East where graduates of this university may not be found.

From the point of view of research, the standard of work of this school is well known to you, in that Prof. Nash and his collaborators have been responsible for a number of publications dealing with their original investigations which have appeared in the journals of several learned societies on both sides of the Atlantic.

The exigencies of time and space prevent my survey being anything but superficial and, indeed, sketchy. It has been my particular and especial good fortune to have been associated with a great company distinguished by its liberal and broad-minded policy towards research. It has been my good fortune to have had the backing and support and encouragement of the chairman of the board. It has been my good fortune to have had a group of colleagues whose aptitude and keenness and loyalty have been beyond all praise, and to have seen so many of them taking a prominent place in our science. Most of all do I count myself lucky to have been born in the "petroleum age."

INSULIN

The application of the Association of British Chemical Manufacturers on behalf of the British Drug Houses, Ltd., Boots Pure Drug Co., Allen & Hanburys, Ltd., and Burroughs, Wellcome & Co., to include insulin in the list of articles dutiable under the Safeguarding of Industries Act, was heard on November 18 and 20 by a Board of Trade Tribunal presided over by Mr. Henn Collins, K.C., sitting with Prof. F. G. Donnan and Prof. Samuel Smiles.

Mr. Trevor Watson, K.C., representing the A.B.C.M., declared that only 1% of insulin on the market was imported and his clients had no intention of raising the price if a duty were imposed. Mr. R. Moritz, K.C., representing C. L. Bencard, Ltd., importers of Danish insulin, in opposing the application said that 1% was a gross understatement. Evidence as to the nature of insulin was given by Dr. E. F. Armstrong and Prof. R. Robinson. It was announced that the tribunal would probably take some time in arriving at a decision.

SOCIETY OF CHEMICAL INDUSTRY

OFFICIAL NOTICES

Annual Chemical Dinner. November 28, at Hotel Great Central: Chairman—Lord Leverhulme; Chief Guest—Mr. A. P. Herbert. Application for tickets with suitable remittance should be made as early as possible to Mr. F. A. Greene, Chemical Club, 2, Whitehall Court, London, S.W.1. The price of each ticket, including dinner, gratuities, and dance, is 12s. 6d.

Australasian Subscriptions. Australasian members, including those in New Zealand, should all have received notice of the necessity to pay the subscription for 1934. This should be done at once in order to ensure the service of the JOURNAL being uninterrupted, but members are reminded that, during the period of depreciated currency, they may pay the subscription direct to the Society's account at the Commercial Bank of Australia, 273, George Street, Sydney. The Bank cannot entertain correspondence on Society's business but will issue an interim receipt.

The Ramsay Chemical Dinner will be held in th Central Hotel, Glasgow, on Friday, December 8. Recep tion 6.45 p.m. Dinner 7 p.m. Dancing till 2 a.m.

The chair will be occupied by Sir Arthur Huddlestone C.M.G., O.B.E., M.A., the new Director of the Roy Technical College.

Tickets may be had from the Convenor, Mr. John C MacCallum, 10, Midlothian Drive, Glasgow, S.1, an applications must be accompanied by the appropriat remittance, 14s. 6d. each. Students' tickets (limited t 20) 10s. 6d.

Those desiring to stay at the hotel overnight may boo accommodation direct with the Central Hotel on th specially arranged terms of 10s. 6d. for bed and breakfas

Chemical Abstracts. The price to non-members the combined "A" and "B" Abstracts, with one inde is now £6 8s., post free.

NEWCASTLE SECTION

A joint meeting of the Newcastle Section with t Institute of Metals was held in Armstrong College Tuesday, November 14, when Mr. W. E. Ballard re a paper on "Metal Spraying." In the absence the chairman, the vice-chairman, Mr. W. Richards presided. The speaker dealt first with the need for a advantages of sprayed coatings, and went on to descr the three chief systems which employ liquid, pow and wire pistols, making special reference to mod developments of the first and third types, and of spe tools for working in restricted places. The liquid pi sprays only horizontally, is heavy, and the jets s burn out, but molten metal is cheap and the pi requires only coal gas at mains pressure and air 60—80 lb.

Wire pistols cover rather more slowly, but t phosphor-bronze or iron easily. The process requ special treatment of the surface beforehand, and sa blasting has a great influence on the adhesion of metal. Unless a rough surface is produced with ang flint or angular shot, adhesion is not satisfactory.

The properties of the sprayed coatings were then described. The metal shows a curious ring-like structure which would be produced by any projectile travelling at about 760 m.p.h. For this reason the deposit must be fairly thick ($\frac{4}{1000}$ to $\frac{6}{1000}$ for soft and $\frac{10}{1000}$ for hard metals) unless porosity is no disadvantage. No heating effect is produced, even gun-cotton having been coated.

Zinc is largely sprayed as a form of galvanising for large objects, vessels for acetate silk manufacture, aviation spirit tanks, anchors, and similar objects exposed to sea-water, and aero-engine parts, screws, overhead grid transmission towers, etc. The surface is an ideal base for paint and is finding application on motor-car bodies for that reason.

Lead can only be sprayed with risk to the operator and so is avoided except for ships' propellers as it is stable to foaming sea-water. Aluminium resists sulphur dioxide, and with heat-treatment can form a protective alloy with iron surfaces. Phosphor-bronze, nickel, and iron can also be sprayed.

In outlining the directions of future development, the lecturer said that metal-spraying afforded not only good protection but a unique way of depositing mixed metals as distinct from alloys and that the properties of such mixtures might be important.

The talk was fully illustrated with slides showing applications of zinc, lead, tin, aluminium, and other metals. The thanks of the meeting to the lecturer were expressed by Mr. Craggs and Mr. Pearson.

NOTTINGHAM SECTION

The first meeting of the session of the Nottingham Section was held on November 2, at the University College, Nottingham, at which there was a large attendance representative of the chemical and other industries of the Nottingham district. Mr. Leonard Anderson, M.Sc., A.I.C., manager of the Fine Chemical Department of Boots Pure Drug Co., Ltd., and chairman of the Section, presided.

Mr. Anderson thanked the Section for his election to the chairmanship and then proceeded to give his inaugural address on "Erection and Lay-Out of Chemical Plant," which was illustrated by photographs of typical British and German chemical and pharmaceutical factories.

After referring to the difficulties arising from haphazard installation and extension of chemical manufacturing processes, Mr. Anderson gave as an example of an ideal factory, the Leverkusen works of the I. G. Farbenindustrie, where fitness for purpose was the main consideration. Here at Leverkusen, a hitherto rural area, complete new works were erected, where every detail, including handling raw materials and products, their transport to and from and within the works, is carried out according to a carefully devised scheme. The scheme includes the most advantageous disposition of the works with regard to river and rail transport and also of the dwellings for housing the staff and employees of the company.

As an example of a modern factory for the preparation, packing, storing, and despatching of pharmaceutical products, Mr. Anderson instanced the new steel and glass factory of Boots Pure Drug Co., Ltd., at Beeston, Nottingham. This factory is unique in its construction as the processes and all the various operations for packing and despatching were first designed and laid out, after which the architects were asked to design a building to cover the works.

Mr. Anderson went on to describe the principles involved in transferring to a manufacturing scale processes which on a small scale were simple bench operations, such as the manufacture of chloroform, the recrystallization of Glaubers salt, and the dissolving of metals for the preparation of various metallic salts. The plant necessary for biochemical processes such as the manufacture of insulin and liver extract were next described. All the plants used in the various chemical operations were carefully constructed from the most suitable material for the job; in one case all the pipes, cocks, and stirring gear were made of silver; in another aluminium was used and for the absorption of hydrochloric acid British stoneware was now giving great satisfaction.

Mr. Anderson was careful to draw attention to the importance of the lay-out with regard to the position of controls, gauges, and heights of outlets from the ground, so as to assure convenient and safe working conditions.

The necessity for the different services such as refrigeration, vacuum, steam and compressed air involved the erection and maintenance of steam power plant, refrigerators, and electrical generators. As a large-scale operation requiring many of these services, he instanced the manufacture of saccharin from toluene and chlorsulphonic acid. The address was illustrated by an excellent selection of specially taken slides of operations as carried out in the Fine Chemical Department of Boots Pure Drug Co., Ltd.

In the discussion which followed, Dr. Pyman congratulated the lecturer on his magnificent set of lantern slides and the lucid way in which he had put the various points which were all of great importance, especially to the younger members of the Section. Mr. Alliott and Mr. Calam also took part in the discussion. A special point raised was that British-made stoneware and enamelled iron vessels could now be obtained as good as any in the world. A vote of thanks to the lecturer was proposed by Dr. Firth of the University College, Nottingham.

CHEMICAL SOCIETY

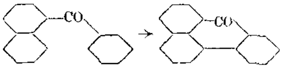
The ordinary scientific meeting on November 16 was devoted to a discussion on "Condensed Aromatic Ring Systems." The President, Prof. G. T. Morgan, O.B.E., F.R.S., occupied the chair.

Dr. R. Fraser Thomson opened the discussion with the following paper:

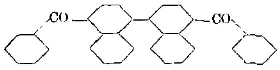
No apology need be made, in a discussion on such a wide subject, for confining the opening remarks to a small branch of the subject which has proved to be an important one in dyestuffs technology. The opening remarks will therefore be centred round the formation of complexes which are derivatives of pyrene and perylene. The reactions deal with aromatic rings throughout and there is no intermediate hydroaromatic stage; also there is always a pair of carbonyl groups in

the final product which are suitably related in order to give vat-dyeing properties.

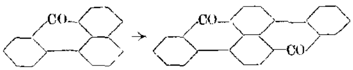
The greatest developments have been made by technologists since the discovery of dimethoxydibenzanthrone (Caledon Jade Green) gave such a fillip to research. *One class of reaction which in general leads to* the type of substance referred to is Scholl's peri-ring-closure, in which benzoyl groups attached to peri positions in naphthalene derivatives are made to form a new benzene ring by the action of aluminium chloride.[1] Thus phenyl α-naphthyl ketone and its derivatives give benzanthrone and its derivatives :



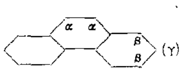
whilst certain more complex cases were also investigated by Scholl, such as dibenzoyl-α-dinaphthyl



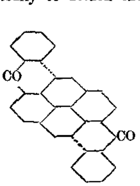
which yields dibenzanthrone[2] by the same method, and is of importance in deciding the structure of this substance. *A technically valuable case is the formation* of dibenzopyrenequinones from benzanthrone.[3] This proceeds through Bz.1-benzoylbenzanthrone, but is technically accomplished in one step



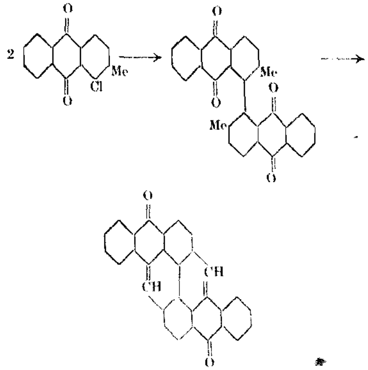
Here it is interesting to note that yields are considerably increased if an oxidising agent is employed in the aluminium chloride fusion, *e.g.*, oxygen or chlorine.[4] The same substance can be obtained from 1 : 5-dibenzoylnaphthalene, but this method is probably only of academic interest.[5] If this general method be applied on paper to other hydrocarbons, it gives interesting results. Thus pyrene



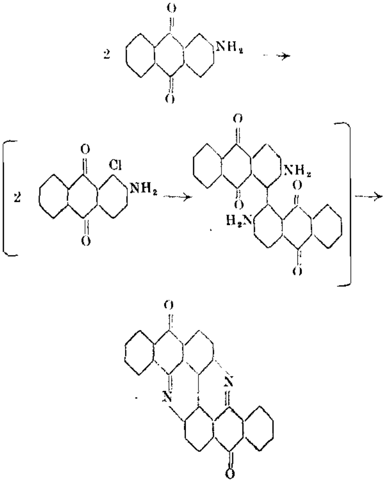
has four pairs of peri-positions, and three different types of carbons (α, β, γ). If two benzoyl groups can be made symmetrically to attack the β carbons, pyranthrone results :



This is not the technical method of manufacture, however, which proceeds from 1-chloro-2-methylanthraquinone by an Ullmann and potash fusion :



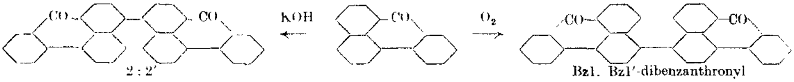
In passing it is interesting to note that flavanthrone, which is produced by the action of antimony pentachloride on 2-amino-anthraquinone, the mode of formation being probably similar to that of pyranthrone,



differs from the latter only in that –N= replaces –CH=. The colours and properties of the two substances are very similar and the relationship is like that of the

porphyrin pigments and the phthalocyanine pigments recently described by Linstead[6] at the British Association.

In the preparation of perylene the first step is the oxidation of β-naphthol to the dinaphthol. The next stage is an aluminium chloride fusion to give dihydroxy-perylene. This step only proceeds well in presence of sodium carbonate.[7] On the other hand benzanthrone can be made to yield either the Bz1 : Bz1'- or the 2 : 2'-dibenzanthronyl according to whether one works in acid oxidising[8] or mild alkaline[9] reducing medium.

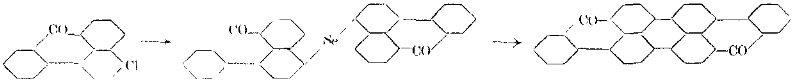


The former does not readily close the Bz1 : Bz1'-position in alkali, while the latter readily does so to give dibenzanthrone. *On the other hand the former in acid-oxidising medium readily introduces the dibenzanthrone* link and two hydroxy-groups in the Bz2 : Bz2'-positions as well. The latter can also be obtained by acid oxidation of dibenzanthrone; the dimethyl ether is Caledon Jade Green. The special activation of the two *peri-positions and their distinguishing characteristics is* particularly noteworthy.

A further remarkable reaction is the transformation of Bz1 : Bz1'-dibenzanthrone sulphide[10] or selenide[11] to very pure *iso*dibenzanthrone; the sulphide or selenide *is prepared from Bz1'-halogenobenzanthrone. The* latter also gives *iso*dibenzanthrone on potash fusion but in very inferior yield.

these vat colours were manufactured on a large scale and employed in dyeing many thousand yards of textile fabrics. The next step was the formation of the Solway *Dyes Co., afterwards Scottish Dyes, Ltd. of Carlisle* and Grangemouth. In the research laboratories of the latter company were conducted those investigations which in 1920 led to the discovery of Caledon Jade Green. Later on, in 1925, this and other vat dyes were *placed on the market in a soluble form under the title* of "Soledon Dyestuffs."

These historical facts should assist British chemists in dispelling the inferiority complex which still besets them when comparing their achievements with those of *their German contemporaries. For those who suffer in* this way, Caledon Jade Green is not only one of the fastest known vat dyes but also an excellent tonic.



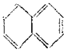
This mechanism is as yet imperfectly understood, as even 2 : 2'-dibenzanthronyl and benzanthrone itself under suitable conditions yield *iso*dibenzanthrone,[12] contaminated more or less with dibenzanthrone.

The President remarked that it was worth while for all British chemists to remember the circumstances in which these important advances in the chemistry of aromatic ring systems had been accomplished. In the year 1913 the British exportation of dyed textiles had reached a very high level, but in those days industrialists engaged in the textile trades were apparently unconcerned about the source of dyes which they then employed. Actually, these dyewares to the extent of 80% were of Continental origin and mainly came from Germany. With the onset of the World War this supply stopped and certain of the fastest vat dyes became unprocurable. Among the firms most hardly hit by this embargo was the Morton Sundour Fabrics, Ltd., an undertaking which, with a world-wide reputation, had grown to be almost entirely dependent on Germany for the vat dyes required in the dyeing of textiles with light resistant colours. Mr. James Morton, the moving spirit in this enterprise, was faced with two alternatives, either to close down or to find another source of fast dyes. He chose the desperate expedient of endeavouring to make the complex vat dyes for himself. With no previous experience in this manufacture he gathered round him a group of chemists, including Dr. Fraser Thomson and the late Dr. J. Thomas, and inspired them with his enthusiasm for the formidable task of manufacturing, under war conditions, dyes which German specialists had prophesied that no British firm would produce within 10 years. So successful were these efforts that in November, 1914, indanthrene blue and indanthrene yellow (flavanthrone) were obtained in the laboratory and during the following year

Prof. G. R. Clemo said: Dr. Fraser Thomson's opening has shown how complex dyestuffs can be made from naphthalene and anthracenes, both obtained from the carbocyclic structure in coal, which originates in all probability from plant ulmins and lignins. The direct production of carbocyclic structures in plants from carbohydrates is not favoured by plant physiologists, although Klason (1931) postulated the formation of lignin from xylose. Amongst the other possible precursors are methylglyoxal, pyruvic acid and glycerol which, dehydrated to give αγ-propylene glycol, is claimed by Freudenburg as giving rise to lignin, and thus ultimately by the reactions just depicted to colours like Caledon Jade Green.

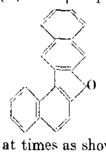
The mechanism underlying the linear or angular attachment of new rings to give condensed aromatic ring systems is very imperfectly understood, although the new ring appears to condense on to a double bond and Nature seems to favour the angular alignment of rings.

Pauling (J. Chem. Phys., 1933, 365) gives "42 canonical structures contributing to the normal state of the naphthalene molecule" with (A) and (B) of about

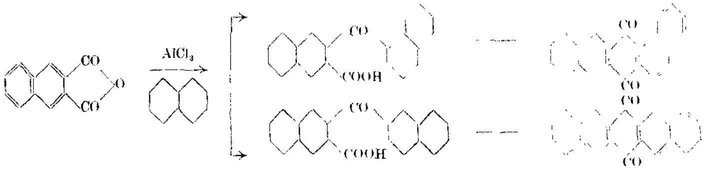
(A)  (B)

equal energy content as numbers 1 and 2 on the list.

It is comforting to find β-naphthylamine undergoing the *Skraup reaction giving exclusively the angular* product based on (A). In β-naphthol however the β′

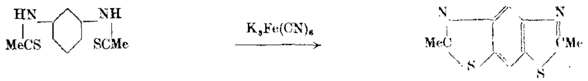


position is reactive at times as shown by our production some years ago of the *iso*dinaphthylene oxide. Again, Waldmann (Ber., 1931, 1713) showed that naphthalene, under mild conditions, can react as both (A) and (B).

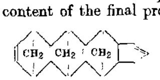


Tetralin is even more dynamic, although Lindner (1927) claims that the (A) form is less strained than (B). *It is stated that ar-tetrahydro-β-naphthylamine gives* 65% of the angular and 35% of linear base in the quinaldine reaction, but 36% of angular and 64% of linear in the Skraup reaction.

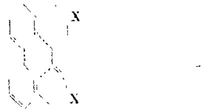
The acetyl derivatives of *ar*-tetrahydro-β-naphthyl*amine and ar-tetrahydro-β-naphthol*, however, react wholly in the (A) form with bromine giving the α-bromo-compounds (cf., Mills, J., 1930, 2510). The literature contains many references to the formation of linear compounds when the angular might have been expected, as in the almost exclusive production of the dithiazole—



The important work of Clar during the past three years, based on the assumption that hydrocarbons exhibit valency tautomerism, does not appear as yet to help much on the question of the mechanism of ring extension. Doubtless, many factors bear on the question and not least the energy content of the final product. The fact



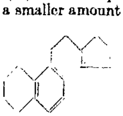
that phenanthrene has 1693 kg-cal. per g.-mol. to the 1695 of anthracene would appear to indicate that the energy factor does not play a decisive part in determining whether the (A) or (B) forms above undergo reaction. If Diels is correct in his claim that the tetra-polymer of *cyclo*pentadiene has the highly strained structure with its corresponding high energy content, one is tempted to ask whether the *product of a reaction really* has less energy than the other possible isomers which might have been formed.

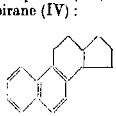


In connexion with perylene, it might be interesting to point some resemblance to the interesting polyenes prepared *by Kuhn. Thus, considering only the fully-*ruled part of the molecule, we might expect perylene *to show some of the properties of diphenyloctatetraene*, such as forming a dipicrate at the double bonds X. It would be interesting to know whether perylene easily forms a dihydro-derivative on reduction. With regard to cholesterol and related problems, it is interesting to recall that it is not definitely classed as of terpene origin at present. So far, the simplest hydrocarbon obtained *from it by Se dehydrogenation is the puzzling methyl*-phenanthrene*cyclo*pentene. In contrast with this is the fact that many complex C_{30} compounds, not far different in empirical formula from cholesterol, which are probably of isoprene origin, such as betulin, oleanolic acid and so on, give simpler $C_{12}H_{12}$, $C_{13}H_{14}$ and $C_{14}H_{16}$ hydrocarbons.

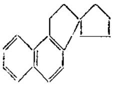
Dr. J. W. Cook [with C. L. Hewett and G. A. D. Haslewood] *said :—The application of Diels's selenium* dehydrogenation method permits of the synthesis of condensed aromatic systems by cyclisation of aromatic compounds with a suitably disposed ethylenic bond a reaction which leads primarily to hydroaromatic compounds. This method was recently used (J.C.S. 1933, 1098) for the synthesis of 1 : 2-*cyclo*penteno phenanthrene. The ring-closures *involved in this* reaction have now been more fully investigated, and it has been shown that cyclisation of 1-(β-1′-naphthyl-ethyl)-Δ^1-*cyclo*pentene (I) gives as the chief products a mixture of 1 : 2-*cyclo*pentano-1 : 2 : 3 : 4-tetrahydro-

phenanthrene (II) and the *spirocyclic* compound (III), together with a smaller amount of the spirane (IV):

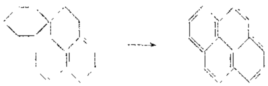

(I)


(II)

(III)

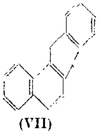

(IV)

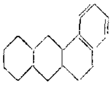
(II) is converted by dehydrogenation into 1 : 2-*cyclo*pentenophenanthrene, which, if the dehydrogenation is carried out with selenium, is contaminated with a hydrocarbon, $C_{17}H_{12}$; this was isolated by Kon (J.C.S., 1933, 1087) in a relatively pure state (m.p. 182—183°). This hydrocarbon, for a specimen of which we are indebted to Dr. Kon, has been identified as chrysofluorene (VII), which evidently arises from (IV) by a rearrangement of the type demonstrated by Clemo and Ormston (J.C.S., 1933, 352) in the case of *cyclo*hexyl-*spirocyclopentane*. *The substance to which structure* (III) is now assigned was formerly regarded as the *trans* isomer of (II). This is incorrect, for nitric acid oxidation gives 4-nitrohemimellitic acid and the completely analogous hydrocarbon (V) obtained from 1-(β-1'-naphthethyl)-Δ^1-*cyclo*hexene gives no chrysene when heated with selenium; it is very resistant to the action of selenium which, however, ultimately leads to pyrene (VI) by rearrangement with loss of two carbon atoms:


(V) (VI)

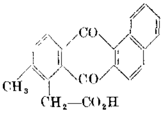
The properties of the hydrocarbon, $C_{17}H_{12}$, obtained by selenium dehydrogenation of (III) leave little doubt that this is 1-methylpyrene.

This type of cyclisation method is also applicable to other condensed-ring systems. Thus, the phenylethylindene obtained by dehydration of the carbinol arising from 1-hydrindone and β-phenylethylmagnesium chloride was converted into a tetracyclic hydrocarbon which was dehydrogenated to chrysofluorene (VII). Also, 2-β-phenylethyl-*trans*-2-decalol is dehydrated to a mixture of octalins, converted by aluminium chloride to saturated isomerides from which the highly crystalline dodecahydro-1 : 2-benzanthracene (VIII), m.p. 71—72°, was isolated and dehydrogenated to 1 : 2-benzanthracene.

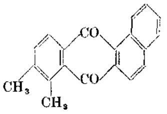

(VII)


(VIII)

The conversion of sterols into aromatic compounds presents several points of interest. The problem of the constitutions of the two hydrocarbons isolated by Diels, Gädke and Körding (Annalen, 1927, **459**, 1) has not yet been completely solved. The identity of the simpler of the two hydrocarbons, "$C_{18}H_{16}$" with 1 : 2-*cyclo*pentenophenanthrene, which was suggested by a preliminary comparison, has not been confirmed by more exhaustive tests. Prof. O. Diels kindly examined a sample of our synthetic 1 : 2-*cyclo*pentenophenanthrene and found that it did not give the characteristic nitrogenous derivative of the hydrocarbon from cholesterol, and Dr. J. D. Bernal had found significant differences in the dimensions of the crystal cell. The dehydrogenation of cholesterol is attended by complications due (*a*) to the lability of the side-chain, (*b*) to the tendency to form a fifth ring, and (*c*) to the presence of a terminal five-membered ring which is liable to rearrange. These complications have been avoided by selecting a bile acid derivative in which the side chain has been utilised in the formation of a new ring, prior to the dehydrogenation. Such a compound is found in Wieland's dehydronorcholene, and the constitution of its dehydrogenation product, methylcholanthrene (Wieland and Dane, Z. physiol. Chem., 1933, **219**, 240: Cook and Haslewood, Chem. & Ind., 1933, **52**, 758) has now been experimentally determined. The quinone-acid formed by oxidation of methylcholanthrene is represented by the structure (IX), for its product of decarboxylation is 5 : 6-dimethyl-1 : 2-benzanthraquinone (X), which is converted by oxidation to anthra*quinone-1 : 2 : 5 : 6-tetracarboxylic acid, identical with* that formed by oxidation of 1 : 2 : 5 : 6-dibenzanthraquinone (comparison of methyl esters).



(IX)

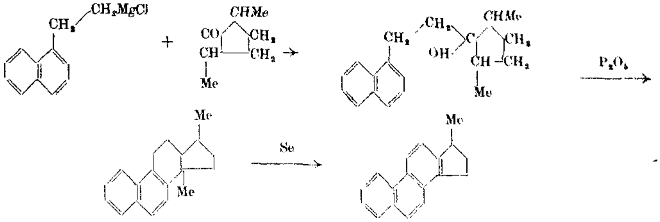


(X)

These results provide additional confirmation of (*a*) the general correctness of the Rosenheim and King sterol formulation, (*b*) the attachment of the side-chain to C_{17} of the sterol ring-system, (*c*) the five-membered nature of ring (IV), and (*d*) the position of the carbonyl group in 12-ketocholanic acid and hence of one hydroxyl group in deoxycholic acid.

Dr. G. A. R. Kon said: A preliminary attempt to prepare 3-methyl*cyclo*pentenophenanthrene, by the condensation of β-(α-naphthylethyl)-magnesium bromide with 2-methyl*cyclo*pentanone, followed by dehydration with phosphoric oxide and dehydrogenation of the cyclic product with selenium, failed because the methyl-bearing carbon atom takes part in the ring-closure and the final product is *cyclo*pentenophenanthrene. The

iifficulty has been overcome by using 2 : 5-dimethyl-*cyclo*pentanone, as follows :



In this synthesis, unless some profound change takes place in the dehydrogenation process, the desired hydrocarbon must be produced.

The new hydrocarbon and its addition complexes with picric acid, trinitrotoluene, and trinitrobenzene have been found to be indistinguishable from Diels's hydrocarbon and its derivatives in appearance and melting point. The absorption spectra of the two hydrocarbons, measured by Dr. R. K. Callow and Mr. F. A. Askew, also agree very well, whilst appreciable differences are observed when these are compared with the spectrum of *cyclo*pentenophenanthrene.

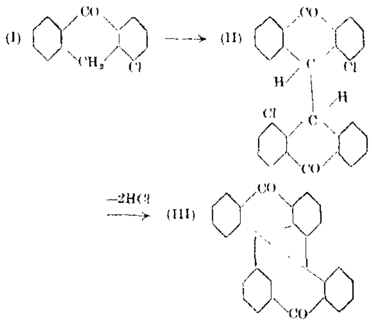
The crystal structure of Diels's hydrocarbon has been studied by Dr. J. D. Bernal, using the *X*-ray method, on a very pure specimen, lately prepared by Prof. Diels, and found to agree within the limits of experimental error with that of the synthetic compound ; the trinitrotoluene compounds were also found to be indistinguishable.

The question of the identity of the new hydrocarbon with Bergmann and Hillemann's preparation (Ber. 1933, 66, 1302) has not yet been settled, although the preparation has been repeated ; there is some evidence to show that the two compounds may be different.

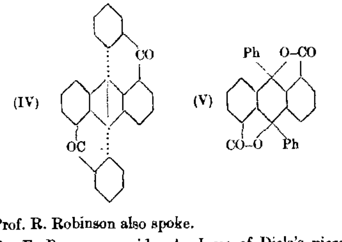
As soon as sufficient quantities of material have been prepared, it is hoped to send a specimen to Prof. Diels, who has promised to prepare the characteristic nitro-derivative $C_{18}H_{13}O_2N$.

In reply to Prof. Robinson, Dr. Kon said that he had no suggestion to make as regards the mechanism by which the hydrocarbon $C_{18}H_{16}$ was produced from cholesterol and admitted that the migration of the methyl group from C_{13} to C_{17}, as required by the current sterol formulæ, was unique.

Prof. I. M. Heilbron [with F. Irving] said : When 4-chloro-9-anthrone (I) (Burnett and Matthews, J., 1923, 123, 2553) is heated either above its melting point or in *boiling phthalic anhydride solution, a purple dyestuff is* formed which is soluble in the usual organic solvents, giving deep red solutions with intense fluorescence. The dyestuff reduces to a green leuco-compound. As purple dyestuffs of this type are not formed from the corresponding 1-chloro-9-anthrones and, as further condensing agents such as aluminium chloride produce only helianthrone derivatives, it was considered that this new class of dyestuffs was probably a derivative of perylene, that from 4-chloro-9-anthrone itself being 5 : 6 : 11 : 12-dibenzperylene-4 : 10-*quinone (III)*. The mechanism of production is rendered clear by the fact that the dyestuff is produced in better yield from 1 : 1'-dichloro-9 : 9'-dianthrone (II), from which 2 mols. of HCl are lost on heating in boiling phthalic anhydride solution :



That formulation (III) is correct has been proved by *the synthesis of the dyestuff from* 1 : 5-dibenzoylanthracene (IV) by means of alkali fusion in presence of an oxidising agent. Further, Scholl, Meyer, and Winkler (Annalen, 1932, 494, 201) have also obtained the same compound from the lactone (V).



Prof. R. Robinson also spoke.

Dr. E. Bergmann said : Analyses of Diels's picrate show that the corresponding hydrocarbon contains 18 rather than 17 carbon atoms. A similar case of the

alleged migration of a methyl group has been found by Ruzicka in the dehydrogenation of alantolactone. In this series of compounds the method of mixed melting points has no value. Jacobs has observed that the dehydrogenation product of strophanthidine gives no depression of melting point with Diels's hydrocarbon, although the former substance gives the analytical figures for a dimethylphenanthrene. In fact, 1 : 2-dimethylphenanthrene gives no depression with *cyclo*-pentenophenanthrene. This indicates at the same time that strophanthidine contains a phenanthrene skeleton similar to that of the sterols and related substances.

Dr. R. D. Haworth said: Two attempted syntheses expected to give 1 : 5-dimethylphenanthrene have yielded 1 : 8-dimethylphenanthrene. The only explanation which we can offer is to postulate a migration of a methyl group *during selenium dehydrogenation.*

REFERENCES

[1] Scholl and Seer, Annalen, 1912, **394**, 143; B.A.S.F., B.P. 16,271/10.
[2] Scholl and Seer, Annalen, 1912, **394**, 171; Seer and Scholl, Annalen, 1913, **398**, 82; B.A.S.F., B.P. 16,271/10.
[3] Mester, Lucius, and Brüning, B.P. 205,502 (12.10.23) and B.P. 220,304 (1.10.24).
[4] I. G. Farbenind. A.G., G.P. 426,711 (9.5.24).
[5] I. G., G.P. 426,710 (21.9.23).
[6] Linstead, *Chemical Trade Journal*, 1933, **93**, 178.
[7] Pereira, B.P. 191,363 (23.10.25).
[8] Scottish Dyes, Ltd., B.P. 251,313 (21.10.24).
[9] B.A.S.F., B.P. 203,533 (19.9.22).
[10] I.G., B.P. 242,620.
[11] Thomson, Anderson, Thornley, and I.C.I., B.P. 367,462 (26.5.30).
[12] Anderson, Thomson, Thomas, and Scottish Dyes, Ltd., B.P. 303,454 (24.6.27); cf. Luttringhaus and Neresheimer, Annalen, 1929, **474**, 280.

BIOCHEMICAL SOCIETY

The twenty-first anniversary meeting was held in the Department of Physiology and Biochemistry, University College, W.C.1, on November 17, 1933. A dinner in celebration of the twenty-first birthday of the Society was subsequently held at the Hyde Park Hotel. The following papers were read:

"The Configurative Relationship of Thyroxine and Tyrosine," by A. Canzanelli, C. R. Harington and S. S. Randall. General chemical and biological considerations have led to the hypothesis that thyroxine is produced in the body from tyrosine through the stage of 3 : 5-di-iodotyrosine: direct evidence in support of this view has however been lacking hitherto. It has now been shown that natural *l*-tyrosine is configuratively related to natural *l*-thyroxine; this finding is believed to constitute the strongest available chemical evidence in favour of the biological relationship of the two compounds.

N-benzoyl-*l*-tyrosine methyl ester was condensed with 3 : 4 : 5-triiodonitrobenzene to give ethyl α-benzamido-β-4-(2′ : 6′-diiodo-4′-nitrophenoxy)phenylpropionate; the corresponding free acid was reduced with ferrous sulphate and ammonia and the resulting amino-compound was de-iodinated by catalytic reduction to give α-benzamido-β-4-(4′-aminophenoxy)phenylpropionic acid. The latter was diazotised and boiled with water, yielding N-benzoylthyronine, which, when hydrolysed with hydrochloric acid, gave *d*-thyronine, $[\alpha]_{5461}$ +13·3°.

l-Thyroxine, previously shown to be identical with the natural compound, was de-iodinated by catalytic reduction and the resulting thyronine had $[\alpha]_{5461}$ +12·2°.

"The Acids Produced from Sugar by a *Penicillium* Parasitic upon *Aspergillus niger*," by John Lewis Yuill. A *Penicillium* with affinities in the *luteum-purpurogenum* group is described which occurs as a parasite on *Aspergillus niger*. It grows over wide ranges of temperature and acidity. In pure culture on cane sugar nutrient solutions at 30° C. with chalk present, it produces an intense blood red colour in mycelium and medium, forms citric acid and a little oxalic acid, both deposited as calcium salts; also the soluble calcium compound of an acid substance insoluble in water but soluble in alcohol. In the same circumstances, but without chalk, neither citric nor oxalic acid are detected, but the insoluble acid in crystalline form encrusts the mycelium and deposits in the solution. This crude material recrystallised yields an acid substance of melting point 201°—202°, insoluble also in petrol but soluble in chloroform, ether, glacial acetic acid, and pyridine.

Microanalysis leads to formula $C_{18}H_{20}O_7$; the substance titrates indefinitely in the cold with NaOH, but on heating gives an equivalent of 87. Heated above its melting point a volatile fragrant substance absorbing bromine is evolved. An acetyl compound melting about 174°, and with C.H. analysis corresponding to a mono-acetyl derivative has been prepared.

The acid appears to be identical with Glauconic acid I derived by Wijkman from cultures of a *Penicillium glaucum* (Leibigs Annalen, 1931, **485**, 61).

"On the Formation of Hyponitrous Acid as an Intermediate in the Microbiological or Photochemical Oxidation of Ammonia to Nitrous Acid," by A. S. Corbet. An investigation of the mechanism of the nitrification of ammonium sulphate has shown that certain of the stages may be effected by microbiological, chemical, or photochemical agency.

The change $NH_3 \rightarrow HNO_2$ may occur as a result of bacterial agency or by the action of light, and in both cases hyponitrous acid is found as an intermediate product. When the transformation is effected by micro-organisms hyponitrous acid may be present in relatively large amount: in one experiment over 50% of the nitrogen was present in this form. The change $HNO_2 \rightarrow HNO_3$ may be the result of bacterial activity or it may take place chemically as the reaction is catalysed by the $H^{\cdot}$ ion. At p_H values below 5·0 the loss of nitrite in this way is not appreciable, but at lower values the loss may be considerable: in a 0·2% solution of KNO_2 at p_H 4·0 the whole of the nitrite was transformed to nitrate in 2 days at 32° C. and in 7 days at 4° C. This is of some practical importance and suggests that, under certain conditions, nitrification in tropical soils may be largely a chemical process. It has also been established that the change $HNO_3 \rightarrow HNO_2$ can take place photochemically.

The evidence for the presence of hyponitrous acid as an intermediate in the oxidation of ammonia is, briefly: a compound intermediate between NH_3 and HNO_2 has been found which is acidic, reduces potassium permanganate, is decomposed on warming in aqueous solution, and is not reduced by Devarda's alloy; the

calcium salt is stable under the conditions of the experiment. With resorcinol and potassium periodate this compound gives a bright orange- to cherry-red coloration which becomes strongly fluorescent. All these properties are possessed by hyponitrous acid, and quantitative estimations support the conclusion that hyponitrous acid is the intermediate compound present.

Although hydroxylamine also gives a reddish colour with resorcinol and potassium periodate, this colour is not fluorescent; moreover, hydroxylamine cannot co-exist with nitrites and it readily reduces Fehling's solution. It has been fonnd that the test for hydroxylamine employed by Blom (Biochem. Z., 1928, **24**, 392) and by Lindsey and Rhines (*J. Bact.*, 1932, **24**, 489), who claim to have detected hydroxylamine as an intermediate product of denitrification, is given also by hyponitrous acid.

"The Estimation of Inositol," by L. Young. The Fleury-Marqne method of estimating polyhydric alcohols, using alkaline potassium iodomercurate, has been adapted for the accurate estimation of inositol in quantities as small as 1 mg.

This has been incorporated in a new method of estimating inositol in biological material which has been successfully applied to brain and heart muscle.

The fresh minced tissue is extracted first with its own weight of acetone, then with 70% acetone, and finally pressed. The combined extracts are filtered, distilled to remove acetone, ether-extracted, and the aqueous residue obtained is subjected to the West-Peterson precipitation. To the hot filtrate, after concentration, solid baryta is added, followed by 4—5 volumes of cold alcohol. The precipitate is filtered, washed with alcohol, decomposed with sulphuric acid, and the filtrate obtained by removal of the $BaSO_4$ concentrated. By the addition of acetone and ether, followed by refrigeration, inositol is precipitated in crystalline form. The crystals are filtered, washed, dried, dissolved in water, and estimated.

Recoveries of inositol added to the tissue are of the order of 95% by this method.

Inositol mixed with twice its weight of glucose can be quantitatively recovered from the solution after complete fermentation of the glucose.

"Studies on the Permeability of Erythrocytes," by Hugh Davson. Ox erythrocytes tend to lose K when suspended in normal serum; in isotonic NaCl they lose K more rapidly; by buffering the NaCl and adding 20 mg. K per 100 c.c. the rate of loss is equal to that in serum. Large increases in K and decreases in Na occur in 1·5% KCl; these changes are uninfluenced by the addition of Ca to the solution. Small losses in K and Na accompany dilution of the serum with H_2O. In isotonic glucose a large loss of Na occurs, appearing to be just as rapid as that observed in KCl. In 1·5% NaCl the corpuscle —Na increases with time, reaching a maximum in 28 minutes. Analysis of the curve of corpuscle —Na against time indicates an initial adsorption of 2·24 millimols. Na per 100 c.c. and then a penetration. A similar analysis of the curve of corpuscle —K against time in 1·5% KCl indicates an initial adsorption and then a penetration, much slower than that of Na in spite of the larger concentration gradient. The simultaneous loss of Na appears to be due to desorption alone.

"The Absorption Spectra of the Vitreous and Aqueous Humours," by E. B. Robertson. Abe (1927) found that the ultra-violet absorption band of the vitreous humour disappeared in a few hours when the liquefied gel was diluted with water or saline, and attributed the effect to the formation of mucoprotein from a precursor. The present work confirms Abe's observation, and shows the aqueous humour to behave similarly. The change is found to be an oxidative one, catalysed by the minute traces of copper present in ordinary distilled water. The band is not due to protein, as previously thought, but its wave-length (265 mμ) agrees closely with that of ascorbic acid (vitamin-C) at the same concentration and p_H. Ascorbic acid is also oxidised in the presence of copper, and appears to be identical with the absorbing substance in the aqueous and vitreous humours, its concentration there being 1—2 mg.% in the ox.

When oxidation is avoided by the addition of cyanide, a value of about 11,000 is found for the molecular extinction coefficient (at 265 mμ) of ascorbic acid in aqueous solution. The value of 7000 found by Herbert and Hirst (1932) is probably accounted for by partial oxidation. On the basis of the above observations, a spectroscopic method is suggested for the estimation of vitamin-C.

CORRESPONDENCE

METRIC MEASURES

SIR,—By some catastrophic occurrence the comma and the "full stop" in the illustrative numbers given at the close of my letter (cf. CHEM. AND IND., November 3, p. 896) have become transposed, so that some may have judged me to be a double-headed Janus.

The examples were intended to emphasize that where in metric notation a comma is universally used to mark the integer from the fraction, and a "full stop" for differentiating the thousands of integers, in all metric countries, including the actual place of birth of what we know as the metric system; on the other hand, the reverse is the practice in non-metric lands, such as ours. Strictly, the name of the unit, or its initial for brevity, should be and frequently is *interposed* between the whole and the fractional parts: thus, 1 gram 249 (or 1,249 if grams are known to be involved) means 1 gram 249 milligrams; whilst 1·249 grams means 1 kilogram 249 grams, when these amounts are read abroad in metric countries. And so they should be in the few countries which are rather Kakotopias than Eutopias in the matter, in order that uniformity should prevail.

As our sailors seem to have managed to make port into starboard, and *vice versa* without accident, the change of stop for comma, and comma for stop, should be within the compass of mere landlubbers. If, as may be believed, our chemists are no less ready of hand and brain than our sailors, it should be possible for them to start a crusade and get the notation aright in this country—at any rate, in scientific literature for a start.

I am, Sir, etc.,
H. E. DURHAM

Dunelm, Hereford
Nov. 22, 1933

PERSONAL AND OTHER ITEMS

We regret to learn of the death recently of Mr. John T. Enequist, president of Seldner & Enequist, Inc. of Brooklyn, New York, in his 75th year. Mr. Enequist was one of the oldest members of the American Section of the Society, having joined the Society nearly forty years ago.

We regret to learn of the death in America, on October 31, of Mr. William Coyne, a director and vice-president of E. I. Du Pont de Nemours, with whom he had been associated since 1904. Mr. Coyne was also a director of Canadian Industries, Ltd. of Montreal, and of the Dunlop Tire & Rubber Co. of Toronto.

Chemical Society: Announcements

It was announced on November 16 that the Council has appointed the following representatives: *Bureau of Chemical Abstracts*: Mr. F. P. Dunn, Mr. A. J. Greenaway, Dr. J. T. Hewitt, Prof. T. S. Moore, and Mr. Emile Mond. Federal Council for Chemistry: Prof. T. S. Moore, Sir William J. Pope, and Prof. J. F. Thorpe. Journal of Physical Chemistry (British Editorial Board): Mr. E. J. Bowen, Prof. W. E. Garner, and Prof. T. M. Lowry.

At the ordinary scientific meeting to be held at University College, Cardiff, on November 24, at 4.30—6.30 and at 7.30 p.m., Prof. G. M. Bennett and Dr. N. H. Hartshorne will open a discussion on "Chemical Applications of Optical and Morphological Crystallography."

The Dyestuffs (Import Regulation) Act, 1920

In the House of Commons on November 8 Dr. Burgin, Parliamentary Secretary of the Board of Trade, stated that the Government had decided to accept the recommendations of the Import Duties Advisory Committee, and a Bill giving effect to the recommendations would be introduced next session. As however there was doubt whether there would be time to pass the Bill in all its stages before December 31, the Government had decided to continue the existing Act for another year. As soon as the changes under the Bill were put into force the Board of Trade would issue a general licence permitting the importation of the goods which the Advisory Committee had recommended should no longer be subject to prohibition. There would be protection for the consumer as recommended by the Committee, and a Joint Committee of Makers and Users would be set up by the Board of Trade.

Food Transport.

A range of insulated containers for the transport of perishable foodstuffs has been designed by R. A Dyson & Co., Ltd., in collaboration with Imperial Chemical Industries, Ltd., and the containers were demonstrated at Thames House on November 20. The insulation employed in "Drikold" on solid carbon dioxide. A full description of the containers will be given later in the JOURNAL.

PATENT LIST

The following is a list of complete specifications of chemical interest which are open for inspection under Section 91 (4) (a) of the Patent Acts. Printed copies are not available, but photographic copies may be obtained at a charge of 6d. per page (minimum 1s.) from the Patent Office, Chancery Lane, W.C.2.

II. 11,757 (1933). Red River Refining Co. Manufacture of lubricating oils.

12,807 (1933). Edeleanu Ges. Purification of liquid hydrocarbons with liquid sulphur dioxide or mixtures thereof.

III. 12,653—6 (1933). Naaml. Venn. Chem. Fabr. Servo, and Rozenbroek. Manufacture of mixed ethers of *higher alcohols and applications of the same for textile* and similar purposes.

IV. 5828 (1933). I. G. Farbenind. Production of azo dyestuffs.

13,025 (1933). I. G. Farbenind. Manufacture of vat dyestuffs.

13,054 (1933). Du Pont de Nemours & Co. Manufacture of azo dyestuffs.

VI. 12,653—6 (1933). Naaml. Venn. Chem. Fabr. Servo and Rozenbroek. *See* III.

VII. 10,343 (1933). Nussbaum. Producing copper sulphate.

X. 11,908 (1933). Verein. Stahlwerke. Preventing coarse crystallization at the solidification of metallic castings.

12,911 (1933). Verein. Stahlwerke. Removing rust from and pickling iron and steel.

13,076 (1933). Grasselli Chem. Co. Pickling of metals and the like processes.

XI. 13,041 (1933). Herbelot. Electrostatic precipitation devices.

13,064 (1933). Glas. Electro-chemical recording.

XIII. 10,936 (1933). Soc. Chem. Ind. in Basle. Manufacture of moulded articles from condensation products derived from aromatic amines and aldehydes.

12,953 (1933). Du Pont de Nemours & Co. Manufacture of resinous products.

12,954 (1933). Du Pont de Nemours & Co. Manufacture of resinous compositions.

XXI. 10,465 (1933). I. G. Farbenind. Multi-colour filters.

13,149 (1933). I. G. Farbenind. Sensitization of photographic emulsions.

MARKET REPORT

This Market Report is compiled from special information received from the manufacturers concerned.

Unless otherwise stated, the prices quoted below cover fair quantities net and naked at sellers' works.

The following alterations in prices are reported since the publication of the last Market Report (cf. CHEM. & IND., Nov. 3, 1933, p. 899).

WOOD DISTILLATION PRODUCTS

Acetate of Lime.—Brown, £9—£10 per ton. Grey, £16—£17 per ton. Liquor, Brown, 30° Tw., 7d.—8d. per gal.

Charcoal.—£6 10s.—£10 per ton, according to grade and locality.

Wood Naphtha.—Miscible, 3s. per gal. Solvent, 3s. 9d.—4s. 9d. per gal.

Wood Creosote.—6d.—2s. 6d. per gal.

TAR PRODUCTS

Toluole.—90%, 2s. 9d.—2s. 10d. per gal. Pure, 3s. 3d. per gal.

PHARMACEUTICAL AND PHOTOGRAPHIC MATERIALS

Menthol.—A.B.R., recryst., B.P., 12s. 6d. per lb. net. Synthetic, 8s. 6d.—12s. per lb. Synthetic detached crystals, 8s. 6d.—10s. 6d. per lb., according to quantity; Liquid (95%), 8s. 6d. per lb.

PERFUMERY CHEMICALS

Rhodinol.—60s. per lb. Safrol.—1s. 6d. per lb. Terpineol.—2s. per lb. Vanillin (*ex Clove Oil*).—14s. 3d.—16s. 3d. per lb.—(*ex Guaiacol*)—14s. 3d.—16s. 3d. per lb.

ESSENTIAL OILS

Peppermint.—Japanese, 4s. 3d. per lb. Wayne County, 13s. 6d. per lb. Petitgrain.—5s. 6d. per lb.